HYDROGEN PEROXIDE

BY

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Monograph Series

REINHOLD PUBLISHING CORPORATION

NEW YORK, N. Y.

CHAPMAN & HALL, LTD., LONDON

Hatcher[...] to be 74 cal./g. or 2510 cal./mole. Foley and Giguère[...] determined the heat of fusion to be 85.83 cal./g. or 2920 cal./mole, using an ice calorimeter and hydrogen peroxide derived from a 99.6% solution many times recrystallized. Both of these results are believed to have been affected by the presence of an uncertain proportion of water. The more precise experiments of Giguère, Liu, Dugdale and Morrison,[23] made with an adiabatic calorimeter and hydrogen peroxide known to contain only 0.03 mole % water, provide the *recommended* value for the heat of fusion of hydrogen peroxide of 87.84 cal./g. or 2987 ± 3 cal./mole. Specific heats for solid and liquid used in this work are detailed later. The accepted value for the heat of fusion of water is 79.72 cal./g. or 1436.3 cal./mole.

Using this datum and the densities of solid and liquid, the slope, dp/dT, of the solid-liquid equilibrium line at the triple point for hydrogen peroxide, $-0.42°C.$ ($272.74°K.$), may be calculated by the Clapeyron equation to be 148 atm./°K. The effect of pressure thus amounts to 0.007°K./atm. and the freezing point under atmospheric pressure is therefore $-0.43°C.$ For water the value of dp/dT is -134 atm./°K. The value of the cryoscopic constant for hydrogen peroxide is similarly calculated to be 1.68°C./mole, compared to 1.86°C./mole for water.

Liquid-Vapor Phase Relationships for Hydrogen Peroxide

In the system water-hydrogen peroxide the liquid components are completely miscible and water is the more volatile to a considerable degree. The system shows negative deviations from Raoult's law; partial pressures of the components in the vapor over the liquid are less than those calculated for ideal solutions. Since there is a large difference in the vapor pressure of the pure components this deviation is not extreme enough to lead to the formation of azeotropes; no vapor pressure minimum or boiling point maximum exists.

The measurement of vapor pressures of hydrogen peroxide and its solutions is complicated by the decomposition that inevitably occurs on heating and concentrating a hydrogen peroxide solution which is not of the highest purity. At the same time the large differences in volatility make for relatively easy concentration in simple equipment of dilute products to the strengths of up to 30 wt. % or higher common in commerce. These facts undoubtedly retarded the undertaking of a precise determination of the vapor-liquid equilibrium relationships of hydrogen peroxide; in the early literature only scattered boiling point data, reported incidentally in studies of concentration techniques, are available.[...] More recent and extended vapor-liquid equilibrium data are given by Sidersky,[70] and Uchida, Ogawa, and Yamaguchi[71] for a limited range of conditions, by Maass and Hiebert[72] and Egerton, Emte, and Minkoff[73] for essentially anhydrous hydrogen per-

oxide, and by Giguère and Maass[2] and Scatchard, Kavanagh, and Ticknor[3] for a wide range of temperature and composition. The agreement among all these sources of data is good, particularly at lower temperatures, but it is believed that the highest degree of accuracy and best experimental procedure were attained by Scatchard, Kavanagh and Ticknor. Their data will be accepted here, and, because of the importance of vapor-liquid equilibrium measurements in establishing many of the properties of hydrogen peroxide-water mixtures, these data and their treatment will be discussed in some detail. Some aspects and calculations are presented that were not given in their paper.

The chief problem to be met in the measurement of the vapor pressure and composition over hydrogen peroxide solutions is the avoidance or allowance for the change in composition or pressure which may be caused by decomposition. In most of the work cited the measurements have been carried out in a static system and some criterion was used for rejection of results or else a means of extrapolation of a pressure-time curve was applied to take into account the effect of the small but important decomposition which occurred in the highly purified hydrogen peroxide samples undergoing test. An alternative technique, which reduces the uncertainty due to decomposition, is to conduct the measurements in a dynamic system allowing continuous boiling under controlled pressure. The experiments of Scatchard, Kavanagh, and Ticknor (and those of the Japanese workers[?]) were performed in such an apparatus. In this procedure there was a continuous production of vapor and subsequent condensation and return of the condensate to the boiler. Within the condenser there was established an interface between the hydrogen peroxide vapor and helium, which was in turn in contact with the mercury in the manometer. The desired temperature was attained by regulating the pressure of helium admitted to the system, and the rate of vaporization was regulated by control of the heat input to the boiler. Assuming that the rate of production of oxygen by decomposition is a function only of temperature and quantity of liquid in the boiler, the partial pressure of oxygen in the vapor space in this apparatus was then determined by the ratio of vaporization rate to decomposition rate, the vapor acting to sweep the oxygen into the helium reservoir. The large volume of this reservoir and the provision of means for periodic adjustment of pressure made it possible to reduce the effect of decomposition on system pressure to negligible proportions. Samples for the determination of liquid composition and temperatures were taken from a secondary or "inner" boiler surrounded by the vapors arising from the primary boiler to which the condensate returned. All vapor passed over a cooling surface for regulating the amount of condensation into the inner boiler and through the liquid in the inner boiler. By proper regulation of the cooling surface a

Table 16. Vapor Pressure of Hydrogen Peroxide-Water Solutions, (from Scatchard, Kavanagh, and Ticknor[14])

Temp. (°C.)	Liquid Composition, mole fraction H_2O_2	Total Vapor Pressure, mm. Hg at 0°C.	Vapor Composition, mole fraction H_2O_2
44.50	0.5140	27.47	0.1273
60.00	0.0905	135.35	0.0054
60.00	0.2038	114.82	0.0104
60.00	0.2810	98.25	0.0307
60.00	0.4075	79.21	0.0839
60.00	0.5823	52.01	0.1757
60.00	0.6831	39.70	0.2051
60.00	0.8423	26.31	0.5699
60.00	0.9910	19.43	0.8072
75.00	0.0745	267.24	0.0036
75.00	0.1972	225.29	0.0107
75.00	0.2777	196.43	0.0207
75.00	0.3241	180.44	0.0408
75.00	0.4800	128.88	0.1070
75.00	0.4903	127.00	0.1114
75.00	0.5751	105.30	0.1834
75.00	0.7460	90.86	0.3907
75.00	0.8572	53.35	0.0381
75.00	0.9596	42.28	—
90.00	0.0904	471.07	0.0080
90.00	0.1054	411.73	0.0235
90.00	0.3257	331.99	0.0450
90.00	0.4080	234.54	0.1342
90.00	0.5118	227.24	0.1516
90.00	0.6546	105.37	0.2716
90.00	0.8418	109.63	0.5082
90.00	0.9507	84.02	0.8858
105.00	0.4985	413.33	0.1404

steady state, i.e., constant level of liquid in the inner boiler, could be attained.

The original data obtained by Scatchard, Kavanagh and Ticknor are presented in Table 16. These authors believed the pressure measurements to be of greater accuracy than the vapor composition measurements, because of fractionation in the boiler and experimental difficulties in maintaining steady state conditions. They have, accordingly, depended solely on the vapor pressure data for the calculation of vapor compositions, extrapolation of the data, and derivation of thermodynamic properties of the solutions.

The method used by Scatchard, Kavanagh and Ticknor for smoothing

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on of the cooling surface)

and extrapolating the vapor pressure data is as follows. It was assumed that the excess free energy of mixing per mole of solution could be represented by an equation of the form:

$$F_x^E = x_w(1 - x_w)[B_0 + B_1(1 - 2x_w) + B_2(1 - 2x_w)^2] \qquad (11)$$

The excess free energy of mixing is defined as the excess or difference between the measured free energy and that defined for an ideal solution. The free energy is in turn related to the chemical potential or partial molal free energy and the activity coefficient by the equations,

$$\mu_a = \frac{\partial F}{\partial n_a} \qquad (12)$$

$$F = \mu_1 n_1 + \mu_2 n_2 \qquad (13)$$

$$\mu_a^E = RT \ln \gamma_a \qquad (14)$$

The total vapor pressure of the solution is then given by the relation

$$P = p_{w_0} \cdot x_w \exp\left(\frac{1}{RT}[\mu_w^E - (\beta_w - V_w)(P - p_{w_0})]\right)$$
$$+ p_{h_0}(1 - x_w) \exp\left(\frac{1}{RT}[\mu_h^E - (\beta_h - V_h)(P - p_{h_0})]\right) \qquad (15)$$

The first additive term is thus the partial pressure of water and the second that of hydrogen peroxide.

After multiplication of equation (11) by the term $(n_w + n_h)$ to express F_x^E in terms of the total moles of solution and differentiation according to equation (12) there are obtained the following expressions for the excess chemical potentials of the components.

$$\mu_w^E = (1 - x_w)^2[B_0 + B_1(1 - 4x_w) + B_2(1 - 2x_w)(1 - 6x_w)] \qquad (16)$$

$$\mu_h^E = x_w^2[B_0 + B_1(3 - 4x_w) + B_2(1 - 2x_w)(5 - 6x_w)] \qquad (17)$$

Equations (16) and (17) may now be substituted into equation (15) and equation (15) fitted to the measured vapor pressures. In fitting this equation to their data Scatchard, Kavanagh, and Ticknor used the following procedure:

(1) The vapor pressure of water was calculated from the equation given by Keyes.[74]

(2) The gas corrections for water were estimated by the method of Keyes, Smith, and Gerry.[x] The corrections for hydrogen peroxide, after estimation of the critical constants, were obtained from the equation recommended for water.

(3) The vapor pressure of anhydrous hydrogen peroxide was obtained,

first by graphical extrapolation of the data for solutions, then from analytical extrapolation of the successive approximations to the equation fitting the experimental vapor pressures.

(4). On the basis of the three foregoing procedures the constants were fitted to the data at each temperature by a successive approximation form of the method of least squares. The constants obtained were then smoothed with temperature, the following values being obtained:

$$B_0 = -752 + 0.97t = -1017 + 0.977T \tag{18}$$

$$B_1 = 85 \tag{19}$$

$$B_2 = 13 \tag{20}$$

The expression for the vapor pressure of unhydrous hydrogen peroxide was obtained in the following manner. Although a linear log p_{A_0} vs. $1/T$ relationship was used within the range of experimental temperatures in the process of evaluating the constants, the log p to $1/T$ relationship for the obvious reference substance, water, deviates appreciably from the simple linear form over large temperature ranges. The Ramsey-Young method of extrapolating vapor pressures was therefore used, with water as a reference substance. The vapor pressure, 17.7 mm. mercury, at 60°C. was used as the reference pressure and the vapor pressure, 78.4 mm. mercury, at 90°C. was used to obtain the difference of the slopes of the log p vs. $1/T$ curves. This difference was found to be -1.5×10^{-5}. A four constant equation was fitted to the derived vapor pressure curve at the temperatures 75, 150, 300, and 450°C. The equation expressing the vapor pressure of anhydrous hydrogen peroxide so obtained was:

$$\log p_{A_0} \text{ (mm.)} = 44.5760 - \frac{4025.3}{T} - 12.996 \log T + 0.0040055\, T \tag{21}$$

With equation (21) for the vapor pressure of hydrogen peroxide, Keyes' equation for the vapor pressure of water, and the values for the constants B_0, B_1, and B_2, a table of partial pressures and of vapor pressures at various temperatures for all compositions of hydrogen peroxide solutions may be prepared. It was believed that the corrections for gas imperfection were of a magnitude comparable to experimental error and that the inclusion of deviations from perfect gas behavior was not warranted in the preparation of an extrapolated table of vapor pressures and vapor compositions. Thus, for this purpose, the terms of equation (15) containing the gas correction factor β were dropped. In terms of the activity coefficient, γ, equation (15) without the gas corrections becomes, by substitution of equation (14):

$$P = p_w x_w \gamma_w + p_{A_0}(1 - x_w)\gamma_A \tag{22}$$

It was assumed that
could be represented

$$(1 - 2x_w)^2] \tag{11}$$

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$$2x_w)(1 - 6x_w)] \tag{16}$$

$$)(5 - 6x_w)] \tag{17}$$

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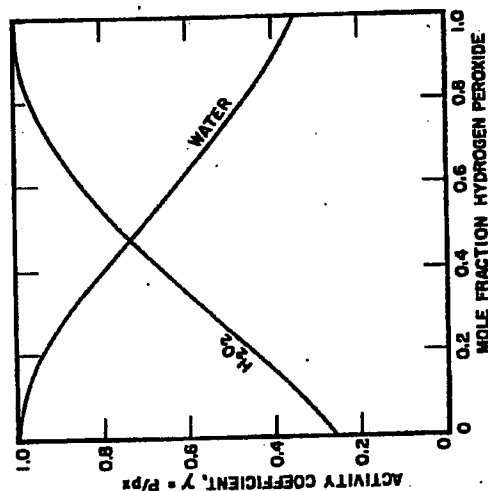| Temp. (°C.)	0.1
0	0.002
10	0.003
20	0.003
25	0.003
30	0.003
40	0.004
50	0.005
60	0.005
70	0.006
80	0.007
90	0.007
100	0.008
110	0.009
120	0.010
130	0.011
140	0.012
150	0.013

It may be seen that t

$$\gamma_w = \exp\left(\frac{(1-x_w)}{RT}\right)$$

$$\gamma_A = \exp\left(\frac{x_A^2}{RT}[B\right.$$

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y_A

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6 PHYSICAL PROPERTIES

FIG. 6—Activity coefficients at 25°C. for aqueous solutions of hydrogen peroxide

ACTIVITY COEFFICIENT, γ = P/px

MOLE FRACTION HYDROGEN PEROXIDE

TABLE 17. TOTAL VAPOR PRESSURE (mm. Hg) OF HYDROGEN PEROXIDE-WATER SOLUTIONS (FROM SCATCHARD, KAVANAGH, AND TICKNOR[85])

T (°C.)	Mole Fraction Hydrogen Peroxide in Liquid										
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	4.58	4.00	3.45	2.81	2.20	1.66	1.21	0.856	0.593	0.404	0.272
10	9.20	8.17	6.96	5.70	4.40	3.42	2.53	1.83	1.30	0.615	0.642
20	17.5	15.0	13.3	10.9	8.60	6.68	5.00	3.66	2.64	1.80	1.36
25	23.7	21.1	18.1	14.0	11.0	0.17	0.00	5.00	3.71	2.60	1.05
30	31.8	28.3	24.3	20.1	16.0	12.4	9.41	6.00	5.14	3.77	2.77
40	55.3	40.3	42.4	35.2	28.3	22.2	17.0	12.8	9.55	7.14	5.35
50	92.0	82.5	71.1	59.3	48.1	37.0	29.3	22.4	17.0	12.0	9.00
60	140	133	115	96.6	78.7	62.0	49.0	37.8	29.1	22.5	17.5
70	234	209	181	152	125	100	79.0	61.8	48.2	37.8	20.8
80	355	318	216	233	192	155	124	97.8	77.2	61.3	40.1
90	520	471	410	348	280	235	180	150	120	96.5	78.2
100	760	682	595	507	422	346	280	225	182	148	121
110	1074	905	845	722	605	490	407	331	260	221	182
120	1480	1330	1175	1008	848	704	578	474	380	322	269
130	2025	1821	1604	1381	1168	974	807	666	552	460	387
140	2700	2443	2153	1860	1580	1326	1105	919	707	645	546
150	3568	3222	2847	2467	2105	1776	1480	1247	1048	887	755

TABLE 18. VAPOR COMPOSITION (MOLE FRACTION H_2O_2) OVER HYDROGEN PEROXIDE-WATER SOLUTIONS, (FROM SCATCHARD, KAVANAGH, AND TICKNOR[56])

Temp. (°C)	Mole Fraction Hydrogen Peroxide in Liquid								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.002	0.006	0.015	0.031	0.060	0.112	0.202	0.352	0.000
10	0.003	0.008	0.018	0.037	0.070	0.128	0.224	0.381	0.026
20	0.003	0.009	0.020	0.041	0.077	0.138	0.238	0.397	0.040
25	0.003	0.010	0.022	0.044	0.081	0.144	0.247	0.407	0.048
30	0.003	0.010	0.023	0.046	0.086	0.151	0.255	0.417	0.050
40	0.004	0.012	0.026	0.052	0.094	0.163	0.272	0.435	0.071
50	0.005	0.014	0.030	0.057	0.103	0.175	0.287	0.452	0.084
60	0.005	0.015	0.033	0.063	0.111	0.187	0.302	0.463	0.690
70	0.006	0.017	0.036	0.068	0.120	0.199	0.310	0.482	0.707
80	0.007	0.019	0.040	0.074	0.128	0.210	0.320	0.495	0.710
90	0.007	0.021	0.043	0.080	0.138	0.221	0.342	0.508	0.725
100	0.008	0.023	0.047	0.085	0.144	0.231	0.354	0.519	0.733
110	0.009	0.025	0.051	0.091	0.152	0.241	0.365	0.530	0.740
120	0.010	0.027	0.054	0.097	0.160	0.251	0.376	0.540	0.747
130	0.011	0.029	0.058	0.102	0.168	0.260	0.388	0.549	0.753
140	0.012	0.031	0.061	0.108	0.175	0.269	0.396	0.558	0.755
150	0.013	0.033	0.065	0.113	0.182	0.278	0.405	0.566	0.703

It may be seen that the activity coefficients are expressed as follows:

$$\gamma_w = \exp\left(\frac{(1-x_w)^2}{RT}\left[B_0 + B_1(1-4x_w) + B_2(1-2x_w)(1-6x_w)\right]\right) \quad (23)$$

$$\gamma_h = \exp\left(\frac{x_w^2}{RT}\left[B_0 + B_1(3-4x_w) + B_2(1-2x_w)(5-6x_w)\right]\right) \quad (24)$$

Values of the activity coefficients at 25°C, have been plotted in Figure 6.

The vapor compositions may be calculated from the relation:

$$y_h = \frac{p_h x_h \gamma_h}{P} = \frac{p_h x_h \gamma_h}{(p_w x_w \gamma_w) + (p_h x_h \gamma_h)} \quad (25)$$

The vapor pressures and vapor compositions calculated by the use of equations (22) and (25) for hydrogen peroxide solutions of all compositions in the temperature range 0-150°C. are presented in Tables 17 and 18.* The data of Tables 17 and 18 have been presented in part in Figures 7, 8,

Extension of the tabulated data may be accomplished with these equations or the alternative method," employing a Dühring plot, may be used.

	0.8	0.9	1.0
	0.563	0.404	0.272
	1.30	0.915	0.643
	2.64	1.80	1.36
	3.71	2.60	1.95
	5.14	3.77	2.77
	9.55	7.14	5.33
	17.0	12.0	0.90
	20.1	22.5	17.5
	48.2	37.8	29.8
	77.2	61.3	40.1
	120	98.5	78.2
	182	148	121
	200	221	182
	380	322	260
	552	400	387
	707	645	540
	1048	887	755